CHEMISTRY AND PROPERTIES OF IMIDE OLIGOMERS CONTAINING PENDANT AND TERMINAL PHENYLETHYNYL GROUPS

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Introduction

As part of a continuing effort to develop high performance/high temperature structural resins for aeronautical applications, oligomers containing latent reactive groups have been under investigation.[1] Material requirements include ease of processability, retention of mechanical properties at elevated temperature, and no loss of mechanical properties after exposure to aircraft fluids such as hydraulic fluid, jet fuel, and cleaning fluids. The phenylethynyl group is an ideal latent reactive group. It has a relatively high cure temperature (~350°C) and a large processing window can be obtained with materials possessing the proper glass transition temperature. The thermally cured materials exhibit good retention of mechanical properties at elevated temperatures with no significant loss of properties after exposure to various solvents. To date, the phenylethynyl group has been incorporated either terminal or pendant to a variety of imide oligomers.[2,3] Upon thermal cure, the phenylethynyl group undergoes chain extension, branching and/or crosslinking; however, the final cured product has not been well defined. As an extension of this work, a series of imide oligomers containing both pendant and terminal phenylethynyl groups (PTPEIs) were prepared as a means to improve retention of mechanical properties at elevated temperature while maintaining processability. The PTPEI oligomers were characterized, thermally cured and the cured polymers evaluated as unoriented thin films and adhesives. The chemistry, physical, and mechanical properties of these materials will be discussed.

Pendant and Terminal Phenylethynyl Imide (PTPEI) Oligomers

Imide oligomers with a calculated number average molecular weight ($\overline{M}_n$) of 5000 g/mol were prepared according to Eq. 1. The diamine(s) were initially dissolved in N-methyl-2-pyrrolidinone (NMP) at room temperature under nitrogen. The dianhydride(s) and phenylethynylphthalic anhydride endcapper were subsequently added as a slurry in NMP and the solids content adjusted to 30% (w/w). The solutions were stirred for ~24h at ambient temperature under nitrogen. An aliquot of the amide acid solution was removed and used for inherent viscosity determination and to cast thin films. Toluene was subsequently added to the remaining solution and the mixture heated to ~155°C for ~16h. As imidization occurred the oligomer precipitated from solution. The cooled reaction mixtures were added to water, washed successively in hot water and methanol and subsequently dried at 240°C under vacuum for 4 h.

Films

NMP solutions (~30%(w/w) solids) of the pendant and terminal phenylethynyl amide acid (PTPEAA) oligomers were centrifuged, the decantate doctored onto clean, dry plate glass and dried to a tack free form in a low humidity chamber. The films on glass were dried in flowing air at 100, 225, and 350°C for 1 h each. Unoriented thin film tensile properties were determined according to ASTM D882 using four specimens per test condition.

Adhesive Specimens

Adhesive tape was prepared by multiple coating of 112 E glass with an A-1100 finish with an NMP solution (20 % (w/w)) of PTPEAA and subsequently staged dried to

225°C in a forced air oven after each coat. After the appropriate thickness had been obtained, the tape was dried to 250°C to a final volatile content of ~2%. Titanium (Ti)-to-Ti (6Al-4V) tensile shear specimens with a PASA-Jell 107 (Products Research and Chemical Corp., Semco Division) surface treatment were fabricated in a press at 350°C under pressure (see Table 1) for 1 h. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

Other Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) solutions in NMP at 25°C. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the glass transition temperature (T_g) taken at the inflection point of the ΔT versus temperature curve.

Results and Discussion

A series of PTPEI oligomers were prepared via the amide acid in NMP according to Eq. 1 at a calculated $\overline{M}_n$ of 5000 g/mol. A representative number of oligomers are presented in Table 1. The η_{inh} of the PTPEAA oligomers ranged from 0.21-0.32 dL/g. Aliquots of the PTPEAAs were removed to cast thin films and the remaining solution imidized via azeotropic distillation with toluene. As imidization occurred, the oligomers precipitated from solution. The initial T_g of the uncured oligomers ranged from 223-231°C with crystalline melt temperatures (T_m) ranging from 274-284°C. The exothermic onset and peak attributed to the reaction of the phenylethynyl group occurred at ~350°C and ~410°C, respectively, and is comparable to that of phenylethynyl terminated imide (PETI) oligomers and pendant phenylethynyl imide (PPEI) oligomers.[2,3] After an isothermal cure at 371°C for 1 h in a sealed DSC pan, the T_g increased ~60-80°C.

Unoriented thin films cured in flowing air to 350°C for 1 h exhibited T_gs ranging from 290-318°C and were typically greater than the same materials cured in a sealed DSC pan (Table 2). This phenomenon has been observed previously for PETIs and was attributed to exposure to air in comparison to that of curing the oligomer in a mold or under vacuum.[2] The room temperature tensile strength and modulus were ~20 ksi and 495 ksi, respectively, with ~50% retention of tensile strength and ~57% retention of tensile modulus at 200°C. Similar results were obtained for PETI-5. However, the % elongation to break of the PTPEI films decreased significantly with respect to PETI films and was attributed to the increased crosslink density of the material. The phenylethynyl content of PETI-5 was ~18% while that of the PTPEI materials was ~30%.

One composition, PTPEI-2, was scaled-up for further evaluation as an adhesive. Ti-to-Ti tensile shear specimens fabricated at 350 and 371°C under 100-200 psi for 1 h exhibited similar strengths (~5000 psi) at 23°C with ~50% cohesive failure presumably due to incomapatability of the resin with the PASA jell surface treatment (Table 3). Specimens bonded at 350°C and 200 psi exhibited better retention of room temperature properties when tested at 177°C than those bonded at 100 psi. Lap shear strengths remained unchanged at 177°C with ~80% retention of room temperature properties when tested at 232°C. Specimens tested at 260°C exhibited ~50% retention of room temperature properties and was not unexpected since the T_g of the cured polymer was 289°C. Unstressed lap shear specimens exposed to hydraulic fluid and jet fuel for 72 h at ambient temperature exhibited a slight decrease in shear strengths when tested at 23, 177, and 200°C. However after a 72 h water boil, the

strength decreased ~20% at 23°C and ~25% at 177 and 200°C.

Conclusions

Several new imide oligomers containing pendent phenylethynyl groups and endcapped with 4-phenylethynylphthalic anhydride were prepared at calculated $\overline{M_n}$ s of 5000 g/mol. All of the oligomers formed tough creasable films which exhibited high tensile properties. Titanium tensile shear specimens fabricated from one composition exhibited excellent retention of room temperature properties when tested at 200°C.

References

1. C.E. Sroog, Prog. Polym. Sci., 16, 561 (1991).
2. P.M. Hergenrother and J.G. Smith Jr., Polymer, 35 (22), 4857 (1994) and references therein.
3. J.W. Connell, J.G. Smith Jr., R.J. Cano, and P.M. Hergenrother, SAMPE, 000 (1996).

Table 1: Oligomer Characterization

PTPEI[1]	η_{inh},dL/g [2] (Amide acid)	T_{gi} (T_m), °C[3]	T_{gc}, °C[4]
1	0.32	231 (282)	313
2	0.29	224 (284)	289
3	0.21	223 (274)	310
4	----	224	283
PETI-5	0.27	210 (286)	249

1. 1. 0.85 3,4'-ODA/0.15 DPEB (diamine containing pendant phenylethynyl group) /BPDA/PEPA
   2. 0.7 3,4'-ODA/0.15 APB/0.15 DPEB/ BPDA/PEPA
   3. 0.75 3,4'-ODA /0.15 APB/0.1 DPEB/ BPDA/PEPA
   4. 0.9 3,4'-ODA/0.1 DPEB/BPDA/PEPA
   5. 0.85 3,4'-ODA/0.15 APB/BPDA/PEPA
2. Determined on 0.5% (w/v) NMP solutions of the amide acid at 25°C
3. Determined by DSC at 20°C/min on as-isolated powders on initial scan
4. Cured in a sealed DSC pan at 371°C/1 h

Table 2: Unoriented Thin Film Properties*

PTPEI	T_g, °C	Test Temp, °C	Str., ksi	Mod., ksi	Elong.@ Break, %
1	318	23	20.2	497	10
		177	11.4	322	9
		200	9.9	267	17
2	301	23	20.4	492	15
		177	11.2	307	24
		200	9.9	285	28
3	306	23	20.5	495	20
		177	12.1	296	27
		200	10.7	299	30
4	290	23	18.9	495	12
		177	10.8	301	34
		200	9.2	276	25
PETI-5	270	23	18.8	455	32
		177	12.2	332	83
		200	9.3	278	69

*Films cured in flowing air to 350°C for 1 h

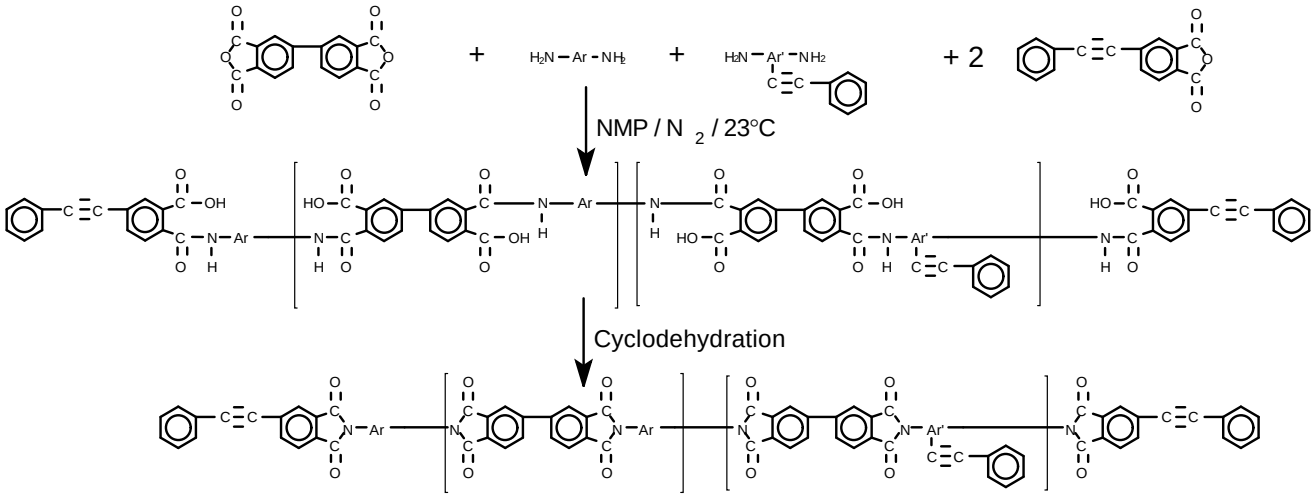
Table 3: Preliminary Adhesive Properties of PTPEI-2*

Processing Conditions (1 h cure)	Test Temp., °C	Str., psi	Failure % C
371°C/200 psi	23	4800	60
350°C/100 psi	23	5200	65
350°C/100 psi	177	4500	100
350°C/200 psi	23	5000	50
350°C/200 psi	177	5000	75
350°C/200 psi	200	4700	90
350°C/200 psi	232	4000	100
350°C/200 psi	260	2600	50

*η_{inh} (PTPEAA, NMP, 0.5%, 25°C,) = 0.30 dL/g, T_g (cured) = 289°C, tape volatile content: ~2%

Table 4: Adhesive Properties of Solvent Exposed PTPEI-2

Solvent Soak, 72 hrs	Test Temp., °C	Str., psi	Failure, % C
Water Boil	23	3900	5
	177	3800	70
	200	3500	80
Hydraulic Fluid	23	4700	15
	177	4300	75
	200	4300	85
Jet Fuel	23	4800	20
	177	4600	80
	200	4400	85



Eq.1